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(54) CATALYST FOR PRODUCING PHENOL AND PRODUCTION OF PHENOL

(57)Abstract:

PURPOSE: To produce phenol from benzoic acid with high selectivity without wastefully using a raw material by adding cobalt oxide to a catalyst for producing phenol by the oxidation of benzoic acid.

CONSTITUTION: A catalyst containing cobalt oxide has high selectivity as a catalyst for producing phenol by the gaseous phase catalytic oxidation of benzoic acid and, by the use of this catalyst, phenol can be produced with high selectivity without forming a high-molecular weight compound such as diphenyl oxide. This catalyst contains cobalt oxide and the proper content of cobalt oxide in the catalyst is within the range of about 0.5-100wt.%. Since the selectivity of phenol lowers when the content of cobalt oxide is below 0.5 wt.%, the pref. content thereof is about 1-100wt.%. Cobalt oxide is supported on a metal oxide carrier composed of titania, magnesia or  $\alpha$ -alumina.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the catalyst for manufacturing a phenol, and the method of carrying out vapor phase oxidation of the benzoic acid under existence of the catalyst, and manufacturing a phenol.

[0002]

[Description of the Prior Art] Conventionally, various approaches and catalysts are known as a catalyst used for the approach and this which carry out gaseous-phase catalytic oxidation of the benzoic acid, and manufacture a phenol.

[0003] For example, the manufacture approach which uses the catalyst which consists of one sort of a copper compound, a vanadium compound, a silver compound, a lithium compound, a sodium compound, and a magnesium compound or two sorts or more, and this catalyst for JP,57-11932,A is indicated.

[0004] Moreover, the manufacture approach which uses the catalyst supported on alpha-alumina in them for JP,59-20384,B including copper, a zirconium, and alkali metal is indicated.

[0005] Moreover, the manufacture approach which uses the catalyst which consists of an oxide which uses molybdenum as an indispensable component, in addition contains at least one sort of at least one sort of PANAJIUMU, niobium, and a tantalum, copper and silver, manganese, iron, cobalt, nickel, a rhodium, palladium, and platinum and at least one sort of a thallium, alkali metal, and alkaline earth metal in JP,64-934,B is indicated.

[0006]

[Problem(s) to be Solved by the Invention] However, the catalyst indicated by JP,57-11932,A had no activity and enough selectivity, and was low also by the manufacture approach which used this catalyst. [ of phenol selectivity ] Moreover, when exothermic reaction like oxidation reaction of a benzoic acid was carried out using the catalyst containing a copper compound, it was easy to produce a hot spot, and sintering of the catalyst by it advanced, and there was a trouble that the fall of activity was remarkable.

[0007] Moreover, the manufacture approach indicated by JP,59-20384,B did not have an invert ratio and enough selectivity, either, and in order that sub\*\*\*\*\*, such as diphenyloxide, might generate mostly, the purification process of a generation phenol was required and it was economically disadvantageous.

[0008] Also in the manufacture approach indicated by JP,64-934,B, an invert ratio and selectivity were low, and it saw industrially and was not enough. Moreover, it was also a problem that diphenyloxide carries out a considerable-amount byproduction and this reduces the activity of a catalyst.

[0009] This invention solves the above trouble and aims at offering the manufacture approach of the catalyst for phenol manufacture with high phenol selectivity, and a phenol.

[0010]

[Means for Solving the Problem and its Function] this invention persons completed a header and this invention for the ability of a phenol to be manufactured with high selectivity, without generating the amount compounds of macromolecules, such as diphenyloxide, by using a header and this catalyst for the catalyst containing cobalt oxide having high selectivity as a catalyst for carrying out gaseous-phase catalytic oxidation of the benzoic acid, and manufacturing a phenol, when it inquires wholeheartedly, in order to attain the above-mentioned purpose.

[0011] That is, the catalyst for phenol manufacture by benzoic-acid oxidization of this invention is constituted considering containing cobalt oxide as a description.

[0012] Moreover, the manufacture approach of the phenol of this invention is constituted in the approach of carrying out gaseous-phase catalytic oxidation of the benzoic acid, and manufacturing a phenol, considering carrying out under existence of the catalyst for phenol composition containing the above-mentioned cobalt oxide as a description.

[0013] The catalyst of this invention contains cobalt oxide and about 0.5 - 100% of the weight of the range is suitable

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for the content of the cobalt oxide as a catalyst. The selectivity of a phenol falls at that content is less than about 0.5 % of the weight. Desirable content is about 1 - 100% of the weight of the range, and about 2 - 100% of the weight of especially its range is desirable.

[0014] Various compounds can be converted into the catalyst of this invention. It is desirable that a transition-metals oxide and a basic compound are added especially. As a transition-metals oxide, an iron oxide, nickel oxide, and chrome oxide are desirable. Moreover, as a basic compound, the compound of alkali metal and alkaline earth metal is desirable, for example, are an oxide, a carbonate, a hydroxide, or nitrates of alkaline earth metal, such as  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{BaO}$ , etc., such as an oxide, a carbonate, a hydroxide, or a nitrate of alkali metal, such as  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Rb}_2\text{O}$ , and  $\text{Cs}_2\text{O}$ , etc. On the other hand, since the amount compounds of macromolecules, such as diphenyloxide, will carry out a byproduction if molybdenum oxide is added, it is not desirable.

[0015] Five or less are suitable for the content of the additive in a catalyst to cobalt oxide at a weight ratio. If there are more contents of an additive to cobalt oxide at a weight ratio than 5, the selectivity of a phenol will fall. Desirable contents are 0.005-1 in the weight ratio to cobalt oxide.

[0016] Furthermore, it can also be used, making catalyst support able to support the catalyst of this invention. As desirable catalyst support, although it is metallic oxides, such as a titania, a magnesia, alpha-alumina, silica gel, a zirconia, tin oxide, and lanthanum oxide, since selectivity is high, a titania, a magnesia, or alpha-alumina is desirable especially. Especially the content of the support in a catalyst has 1 - 95 desirable % of the weight zero to 99% of the weight.

[0017] The gestalten of the catalyst of this invention may be fine particles-like. Mean particle diameter may be 5-60 meshes.

[0018] In manufacture of the catalyst of this invention, the general preparation approach of this kind of oxide catalyst can be used. For example, as for the raw material for manufacture of a catalyst, a nitrate, a carbonate, an organic-acid salt, a halogenide, a hydroxide, etc. are used as a compound of cobalt. Moreover, when using catalyst support, the usual sinking-in technique can be used. Thus, as long as the prepared catalyst constituent has the need, it may be calcinated with a conventional method. As for baking, it is desirable to be 350-800 degrees C in temperature, and to carry out by heating in nitrogen or air for 1 to 10 hours.

[0019] Next, the manufacture approach of the phenol of this invention is explained. Although oxygen is supplied with the benzoic acid of a raw material in this invention, the oxygen to supply has [ that what is necessary is just to be more than the amount of stoichiometries to the benzoic acid of a raw material ] the desirable range of an about 0.5 to 50 time mol, especially an about 0.5 to 5 time mol. When there is more supply of oxygen than an about 50 time mol, the complete oxidation of a raw material benzoic acid becomes easy to happen. Moreover, when there is less supply of oxygen than an about 0.5 time mol, sufficient benzoic-acid invert ratio is not obtained.

[0020] Moreover, although molecular oxygen is sufficient as the oxygen to supply, what air was generally used and diluted this with inert gas may be used.

[0021] It is desirable to perform a reaction to the bottom of existence of a steam. The steam to supply has the desirable range of an about 1 time mol to a 100 time mol to the benzoic acid of a raw material. If there is more amount of supply of a steam than an about 100 time mol, it is not economical, about 1 time, if fewer than a mol, generation of benzene and benzoic-acid phenyl will increase, and the selectivity of a phenol falls.

[0022] The range of reaction temperature of about 200 degrees C - 600 degrees C is desirable, and its range which is about 350 degrees C - 500 degrees C is especially desirable. If reaction temperature is higher than about 600 degrees C, the selectivity of a phenol will fall, and if reaction temperature is lower than about 200 degrees C, a benzoic-acid invert ratio will become low.

[0023] Although there will be especially no limit if reaction pressure is range at which feed maintains a gaseous state under a reaction condition, it is usually in ordinary pressure or some pressurization condition.

[0024] In addition, in the approach of this invention, which equipment of the fixed bed and the fluid bed may be used.

[0025] A purification phenol is obtained by performing the usual after treatment, for example, distillation, after reaction termination.

[0026]

[Example]

I. What dissolved 200.0g ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) of preparation example 1 cobalt nitrates of a catalyst in 500ml of ion exchange water, and the thing which dissolved about 60g of sodium hydroxides in 500ml of ion exchange water were dropped at about 2l. of ion exchange water, maintaining at pH 7-7.5. The filtration and washing of precipitation which continued stirring after dropping termination for about 1 hour, and were generated were performed. And the gel matter

was dried at 120 degrees C among air for 24 hours, and it calcinated at 500 degrees C among air further for 3 hours. The acquired catalyst was  $\text{Co}_3\text{O}_4$ .

[0027] What dissolved 358.9g of example 2 cobalt nitrates in 500ml of ion exchange water, and the thing which dissolved about 110g of sodium hydroxides in 500ml of ion exchange water were dropped at about 2l. of ion exchange water, maintaining at pH 7-7.5. The filtration and washing of precipitation which continued stirring after dropping termination for about 1 hour, and were generated were performed.

[0028] Next, the 100ml water solution which contains 4.6g ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) of sodium carbonates in this gel matter was added, and it stirred for about 1 hour. And the gel matter was dried at 120 degrees C among air for 24 hours, and it calcinated at 500 degrees C among air further for 3 hours. The presentation of the acquired catalyst was  $\text{Co}_3\text{O}_4:\text{Na}_2\text{O}=99:1$  (weight ratio).

[0029] An example 3 and 36.3g of 4 cobalt nitrates were dissolved in about 300ml of ion exchange water, and evaporation to dryness of the titania (product [ made from Kanto Chemistry ], anatase mold) 90g was further supplied and carried out to this water solution. And this thing was dried at 120 degrees C among air for 24 hours, it calcinated at 500 degrees C among air further for 3 hours, and the target catalyst was acquired. The presentation of the acquired catalyst was  $\text{Co}_3\text{O}_4:\text{TiO}_2=10:90$  (weight ratio).

[0030] The magnesia (the product made from Kanto Chemistry, reagent chemicals) was used instead of example 5 titania, and the catalyst was prepared by the same approach as examples 3 and 4. The presentation of the acquired catalyst was  $\text{Co}_3\text{O}_4:\text{MgO}=10:90$  (weight ratio).

[0031] Alpha-aluminum  $2\text{O}_3$  (the Sumitomo Chemical Co., Ltd. make, KHT-24) was used instead of example 6 titania, and the catalyst was prepared by the same approach as examples 3 and 4. The presentation of the acquired catalyst was  $\text{Co}_3\text{O}_4:\text{alpha-aluminum } 2\text{O}_3=10:90$  (weight ratio).

[0032] 18.1g of example 7 cobalt nitrates and 25.5g ( $\text{Fe}(\text{NO}_3) 3 \cdot 9\text{H}_2\text{O}$ ) of iron nitrate were dissolved in about 300ml of ion exchange water, and after supplying and carrying out evaporation to dryness of the titania 90g to this water solution further, it dried at 120 degrees C for 24 hours, and calcinated at 500 degrees C among air further for 3 hours. The presentation of the acquired catalyst was  $\text{Co}_3\text{O}_4:\text{Fe}_2\text{O}_3:\text{TiO}_2=5:5:90$  (weight ratio).

[0033] 19.5g ( $\text{nickel}(\text{NO}_3) 2 \cdot 6\text{H}_2\text{O}$ ) of nickel nitrate was used instead of example 8 iron nitrate, and the catalyst was prepared by the same approach as an example 7. The presentation of the acquired catalyst was  $\text{Co}_3\text{O}_4:\text{NiO}:\text{TiO}_2=5:5:90$  (weight ratio).

[0034] 36.3g of example 9 cobalt nitrates and 4.6g of sodium carbonates were dissolved in about 300ml of ion exchange water, and after supplying and carrying out evaporation to dryness of the titania 89g to this water solution further, it dried at 120 degrees C for 24 hours, and calcinated at 500 degrees C among air further for 3 hours. The presentation of the acquired catalyst was  $\text{Co}_3\text{O}_4:\text{Na}_2\text{O}:\text{TiO}_2=10:1:89$  (weight ratio).

[0035] The catalyst was prepared according to the example 1 of a comparison, and the example 1 indicated by 2 JP,64-934,B. The presentation was  $\text{MoO}_3:\text{V}_2\text{O}_5:\text{CuO}:\text{Na}_2\text{O}:\text{aluminum } 2\text{O}_3=3.9:3.7:3.8:5.9:82.7$  (weight ratio).

[0036] The catalyst was prepared according to the example 1 of reference indicated by example of comparison 3 JP,59-20384,B. The presentation was  $\text{CuO}:\text{ZrO}_2:\text{K}_2\text{O}:\text{aluminum } 2\text{O}_3=4.0:3.0:3.6:89.4$  (weight ratio).

[0037] The particle size regulation of each catalyst manufactured by the four to manufacture examples [ of II. phenol ] 10-18 and example of comparison 6 above was carried out to 20-40 meshes, and specified quantity restoration was carried out at the quartz tube with a bore of 20mm. And specified quantity supply was carried out and a benzoic acid, a steam, air, and nitrogen were made to react to this coil at predetermined temperature. In addition, experiment conditions and an experimental result are shown in Table 1.

[0038]

[Table 1]

使用触媒	実施例10	実施例11	実施例12	実施例13	実施例14	実施例15	実施例16	実施例17	実施例18	比較例4	比較例5	比較例6
	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8	実施例9	比較例1	比較例2	比較例3
組成(重量比)	Co <sub>3</sub> O <sub>4</sub> (100)	Co <sub>3</sub> O <sub>4</sub> -Na <sub>2</sub> O (99:1)	Co <sub>3</sub> O <sub>4</sub> /TiO <sub>2</sub> (10:90)	Co <sub>3</sub> O <sub>4</sub> /TiO <sub>2</sub> (10:90)	Co <sub>3</sub> O <sub>4</sub> /MgO (10:90)	Co <sub>3</sub> O <sub>4</sub> / α-Al <sub>2</sub> O <sub>3</sub> (10:90)	Co <sub>3</sub> O <sub>4</sub> - Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> (5:5:90)	Co <sub>3</sub> O <sub>4</sub> -NiO /TiO <sub>2</sub> (5:5:90)	Co <sub>3</sub> O <sub>4</sub> -Na <sub>2</sub> O /TiO <sub>2</sub> (10:1:89)	MoO <sub>3</sub> -V <sub>2</sub> O <sub>5</sub> -CoO-Na <sub>2</sub> O -Al <sub>2</sub> O <sub>3</sub> (3.9:3.7: 3.8:5.9: 82.7)	MoO <sub>3</sub> -V <sub>2</sub> O <sub>5</sub> -CoO-Na <sub>2</sub> O -Al <sub>2</sub> O <sub>3</sub> (3.9:3.7: 3.8:5.9: 82.7)	CoO-ZrO <sub>2</sub> -K <sub>2</sub> O-Al <sub>2</sub> O <sub>3</sub> (4.0:3.0: 3.6:89.4)
使用量(mg)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.9	3.85	5.3
反応温度(℃)	400	400	400	400	400	400	400	400	400	300	300	300
供給安息香酸	2.3	2.3	2.3	1.6	2.3	2.3	2.3	3.6	2.3	2.3	4.0	2.3
ガス	69.8	69.8	69.8	49.2	69.8	69.8	69.8	53.6	69.8	69.9	71.0	69.9
濃度	0.9	0.9	0.9	6.6	0.9	0.9	0.9	1.4	0.9	4.7	5.1	4.7
空速(h <sup>-1</sup> )	27.1	27.1	27.1	42.6	27.1	27.1	27.1	41.4	27.1	23.1	20.0	23.1
安息香酸転化率(%)	3200	3200	3200	4600	3200	3200	3200	2050	3140	2640	9380	2950
72h後	10.0	19.4	9.5	17.8	9.1	8.3	13.0	13.7	21.9	47.8	16.3	25.1
通	85.5	87.6	91.8	86.7	87.4	80.7	83.3	82.0	85.4	79.7	41.3	70.4
択心	5.8	10.9	8.0	12.1	11.3	18.4	16.4	14.7	13.0	2.9	14.2	4.6
CO、CO <sub>2</sub>	6.8	1.1	0.1	1.1	1.2	0.6	0.2	3.9	1.6	16.3	30.5	18.7
72h後材料収率(%)	0	0	0	0	0	0	0	0	0	1.1	13.4	6.1

[0039]

[Effect of the Invention] This invention has the effectiveness that a phenol can be manufactured with high selectivity from a benzoic acid, by using the catalyst containing cobalt oxide. Therefore, by making the benzoic acid which

remained in the reaction recycle, a phenol is [ a raw material ] generable without facility.

[0040] Moreover, there is little generation of CO and CO<sub>2</sub>, and it can use effectively, without burning a benzoic acid.

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